

Ancient Warriors and the Origin of Chinese Purple

In March 1974 during the sinking of wells for farmland irrigation near Xi'an, China, 9 farmers made one of the world's most remarkable archaeological finds: the discovery of an army consisting of more than 8000 life-size terra cotta figures of warriors and horses of the First Emperor of Qin. One of the most intriguing puzzles is the purple synthetic pigments ("Chinese Purple" or "Han Purple" [1]) found on the terra cotta soldiers (figure 1). Until the 19th century, most pigments were based on naturally occurring colored minerals and dyes, with three significant exceptions: Egyptian Blue ($\text{CaCuSi}_2\text{O}_{10}$), Chinese Blue ($\text{BaCuSi}_2\text{O}_{10}$)/ Purple ($\text{BaCuSi}_2\text{O}_6$) and Maya Blue. The former two are alkaline-earth copper silicates, and because of this similarity it has been proposed that the Chinese pigments were derived from Egyptian Blue [2].



Figure 1: (a) Warrior # T18G21-08, a kneeling archer. The pigment samples in this study have been taken from this terracotta warrior. (b) Close-up picture of the purple paint on the terracotta warrior. (c) Images of the purple paint samples used in this study.

This supposition, however, leaves many open questions. First, it is unlikely that the Chinese chemists could have acquired the technology (not just the pigment) from Egypt well before the official "silk road" (125 BC). Some earliest Chinese Purple samples date back to the "Warring States" period (479-221 BC). Considering the time needed to switch a calcium-based technology to a barium-based one, this technology transfer, if there was one, must have happened well before the "Warring States" period. But even if there existed a connection between China and Egypt, it does not explain why the Chinese decided to substitute Ba for Ca and face the challenges associated with the consequent elevation of the synthesis temperature. An additional problem with this theory is that, to our knowledge, no Ca-bearing Egyptian Blue has been found in China.

In our study, we analyzed clumps of pigment (figure 2) from the Qin warriors and discovered that in spite of the structural similarity to Egyptian Blue, the micro-structural morphology of Chinese Purple is very different. Based on the morphology and the phase distribution in the clumps of the

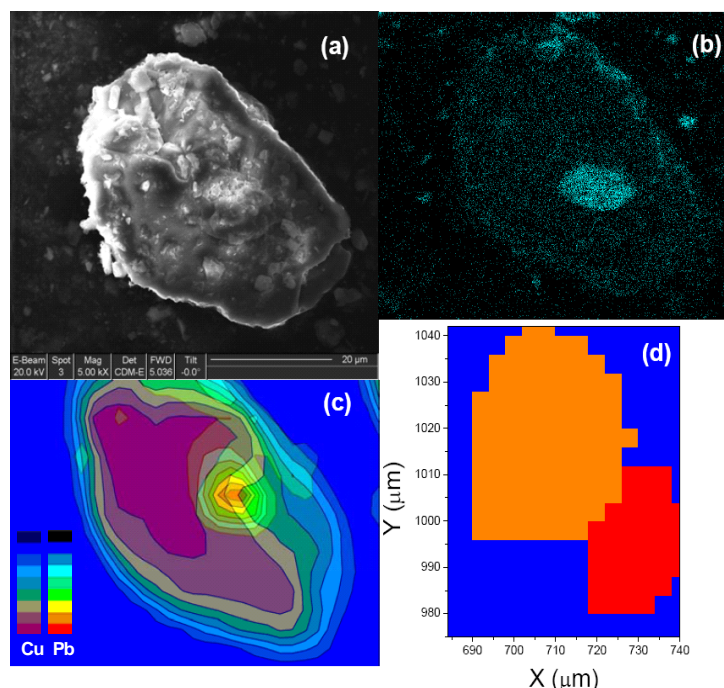


Figure 2: (a) SEM image of the pigment clump taken at 20KeV. (b) Lead ($\text{Pb L}\alpha$) concentration EDX map of the same clump is taken at 15keV. (c) We show an overlapping μXRF ($1.5\mu\text{m}$ spot size) concentration map of Pb (light green, yellow, and orange regions) and Cu (dark green and purple regions) taken at 14KeV. μXRF provides more bulk sensitive information than the EDX microanalysis. (d) The detailed crystallographic map derived from the μXRD ($1.2\mu\text{m}$ spot size) scan. It shows that there are two pigment grains (in orange and red) in the clump which have slightly different crystallographic orientations. The Pb compounds are found either in between the two grains or on the boundary of the grains.

pigment, it appears that the process by which Chinese Purple was synthesized is very similar to that of barium-containing glasses [3] Combining these results with other archaeological evidence, we propose that the synthesis technology for the Chinese pigments was in fact a by-product of high-refractive index glasses (artificial jades) produced by Taoist monks. Furthermore, the disappearance of these pigments from Chinese art and monuments concurrently with the decline of Taoism substantiates the link between the two.

In summary, we argue that Chinese Purple was invented by Taoist alchemists as a by-product of the technology originally developed for synthesizing barium-containing glasses, which, in turn, were invented for the purpose of imitating jade. The barium compounds were added to increase the refractive index of the glass, thus giving the glass a similar appearance as jade. The development of this process also benefited from two well-developed technologies in ancient China: the earlier Bronze making (adding lead compounds to reduce the melting temperature) and pottery making (advanced pottery kilns) technologies.

It is remarkable that three ancient civilizations, Egypt, China and Maya, invented their own blue pigments independently. The evolution of Chinese purple and blue pigments is also a good example of how cultural changes in the society affected the science and technology development in ancient China.

Primary Citation

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